ENEDIOLS FROM 2, 6-XYLIL

BY

SAMUEL LEROY SCOTT

B. S., Illinois Wesleyan University, 1937
M. S., University of Illinois, 1938

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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ENEDIOLS FROM 2,6-XYLIL

INTRODUCTION

The isolation of the solid dienol II as the product of the catalytic hydrogenation of 2,4-di-(mesitoyl)-2,4-pentadiene (I)[1] suggested that enediols of the general type Ar — C(OH) = C(OH) — Ar, being more highly conjugated, might possess still greater stability.

The synthesis of 1,2-dimesityl- (III),[2] 1,2-di-(2,4,6-triethylphenyl)- (IV),[3] and 1,2-di-(2,4,6-triisopropylphenyl) acetylene glycol (V)[4] has proved this to be true.

$$(CH_3)_3C_6H_2COC(=CH_2)-CH=CCOC_6H_2(CH_3)_3 \quad \xrightarrow{H_2}$$

I

$$(CH_3)_3C_6H_2C(OH)=C(CH_3)-CH_2-C(CH_3)=CC_6H_2(CH_3)_3$$
$$\text{OH} \qquad\qquad\qquad\qquad \text{OH}$$

II

$$(CH_3)_3C_6H_2C(OH)=C(OH)C_6H_2(CH_3)_3$$

III

$$(C_2H_5)_3C_6H_2C(OH)=C(OH)C_6H_2(C_2H_5)_3$$

IV

$$(C_3H_7)_3C_6H_2C(OH)=C(OH)C_6H_2(C_3H_7)_3$$

V

The present work was the preparation of similar enediols from 2,6-xylil, $(CH_3)_2C_6H_3COCOC_6H_3(CH_3)_2$, and two of its derivatives, 4,4′-dibromo-2,6-xylil and 3,3′-diamino-2,6-xylil.

EXPERIMENTAL AND DISCUSSION OF RESULTS

The action of the binary mixture, $Mg + MgI_2$,[5] on 2,6-xyloyl chloride led to the formation of 2,6-xylil in yields of 57 per cent. When the reaction was allowed to proceed more than twenty-four hours, a mixture of 2,6-xylil and 2,6-xyloin,

$$(CH_3)_2C_6H_3COCHC_6H_3(CH_3)_2,$$
$$\quad\quad\quad

chloride in methanol rearranged them to 2,6-xyloin. This compound was also obtained by the reaction of 2,6-xylil with phenylmagnesium bromide. It reacted with acetic anhydride to give an acetate, and was oxidized to 2,6-xylil by means of copper sulfate and pyridine.

The reactions of 4,4′-dibromo-2,6-xylil essentially paralleled those described above. Catalytic hydrogenation led to the isolation of two isomeric enediols, as was expected. These enediols differed markedly from the two 1,2-di-(2,6-xylyl) acetylene glycols in their stability. A few minutes' exposure to the air was sufficient to produce a definite yellow coloration, indicating that the *p*-bromine atoms exerted an activating effect on the enediol linkage.

The nitration of 2,6-xylil gave a mixture of 3,3′-dinitro-2,6-xylil, 3,3′,5,5′-tetranitro-2,6-xylil, and a third compound (as yet unidentified) in yields of 92, 1, and 7 per cent, respectively. A slight variation of the conditions has led to a quantitative yield of the desired dinitro derivative. Reduction of this compound gave 3,3′-diamino-2,6-xylil, catalytic hydrogenation proceeding through the intermediate formation of the enediol.

SUMMARY

Two new α-diketones, 2,6-xylil and 4,4′-dibromo-2,6-xylil, and the corresponding xyloins, have been synthesized.

Catalytic hydrogenation of the two xylils led to the isolation of two pairs of stereoisomeric enediols. These were characterized by their diacetates and dibenzoates and by rearrangement to their corresponding xyloins. The bromo substituent was found to decrease the stability of the enediol to a remarkable extent.

2,6-Xylil has been nitrated to give a dinitro derivative. This compound has been reduced to 3,3′-diamino-2,6-xylil, catalytic reduction leading to the intermediate formation of an enediol.

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VITA

The author was born near Rock Falls, Illinois, on November 4, 1917. He attended a rural school near Rock Falls and was graduated from Rock Falls Township High School in 1933. He received the degree of Bachelor of Science from Illinois Wesleyan University in 1937, and obtained the degree of Master of Science at the University of Illinois in 1938. He was the recipient of a University scholarship for the year 1937-1938, and held University fellowships during the years 1938-1939 and 1939-1940.

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